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POLYMERIC ORGANOMETALLICS AS PRECURSORS OF POLYMER SUPPORTED CA--ETC(U)

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This report describes work designed to characterize and systematically explore the chemistry of organometallic derivatives of graphite and polystyrene in order to determine more efficient methods for supported catalyst preparation. The descriptive chemistry of reactive alkali metal-graphite intercalation compounds and in particular the chemistry of potassium-graphite (C ₈ K) is discussed and the results of mechanistic studies of the		

20. Abstract, cont.

reducing ability of potassium-graphite are summarized. The preparation of hydrogenation catalysts from potassium-graphite and palladium (II) complexes is reported, although the nature of these catalysts (i.e. intercalated or supported palladium) has not been determined. Catalytic activity of these catalysts in olefin hydrogenation is comparable to palladium on carbon provided that any excess alkali metal-graphite has been quenched. Methods for lithiation of polystyrene have been surveyed and an analytical procedure based on gas chromatography has been devised for analysis of polymeric organolithium species. This procedure employs the reaction of a 1,2-dibromoalkane with a polymeric lithium reagent to generate the corresponding alkene which is analyzed by gas chromatography. In this reaction, an amount of alkene equal to the amount of lithium species present is generated so that the amount of polymeric lithium reagent can be quantified. A further advantage of this technique is that it distinguishes between polymeric and adsorbed lithium reagents because adsorbed lithium reagents such as n-butyllithium produce other products which can be detected by gas chromatography. Preliminary studies in which lithiated polystyrene is allowed to react with soluble palladium(II) complexes to produce polymer supported olefin hydrogenation catalysts are also described. Finally, the preparation of a new class of organometallic polymer, a polymeric alkali metal radical anion, is described and some aspects of the chemistry of these new polymeric organometallic species are discussed.

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Polymeric Organometallics as Precursors of Polymer Supported
Catalysts

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Polymer supported catalysts have received considerable attention as an alternative to conventional heterogeneous catalysts since a polymer supported transition metal complex often possesses the selectivity of a homogeneous catalyst and the experimental simplicity of a heterogeneous catalyst.¹ In practice, polymer supported catalysts often have additional advantages (and some disadvantages) associated with the polymeric support. The work described here has as its eventual goal the preparation of polymer supported catalysts which have initially been bound to either an inorganic or organic polymer by carbon-metal bonds. The metallic species generated in this fashion would be expected to be reduced during the course of a hydrogenation reaction and could thus be considered to be either immobilized homogeneous metal complexes or true heterogeneous catalysts. This approach to the preparation of a "hybrid" catalyst differs from the conventional procedure followed by most other workers in that the metal species immobilized do not necessarily have a homogeneous counterpart. For example, metal complexes such as rhodium(I) chloride phosphine complexes have been attached to polystyrene using polymer bound phosphine groups and the resulting complexes have been successfully used as hydrogenation or hydroformylation catalysts in a manner not unlike their homogeneous counterparts. An alternative mode of attachment of transition metal catalysts is through a cyclopentadienyl group which has been attached to the polymer. For example, Grubbs and Brubaker have successfully prepared polymer bound titanium catalysts by attachment of bis(cyclopentadienyl)titanium dichloride to polystyrene in this way.²

Our work has concentrated so far on two different types of polymers, graphite and polystyrene. Our general approach has been to attempt to first characterize and more adequately understand

the chemistry of potentially active organometallic derivatives of graphite and polystyrene before attempting extensive catalytic studies. Preliminary studies have, however, shown that active hydrogenation catalysts for simple olefins can be prepared from the polymers we are using. This paper describes both the background chemistry of reactive alkali metal-graphites and metalated polystyrene as well as some initial catalytic data for olefin hydrogenation using catalysts derived from these two types of metalated polymers.

Graphite is an obvious candidate as an inorganic polymer which could be functionalized to yield a catalyst support. Potassium-graphite and other alkali metal-graphites are reactive graphite derivatives which are readily available commercially or are easily prepared by the procedure of Lalancette³ in which stoichiometric amounts of potassium and graphite are allowed to directly react at 100°C with vigorous stirring under an argon atmosphere. This solid-solid reaction works well with potassium, rubidium, and cesium to yield alkali metal-graphites C_nK , C_nRb , or C_nCs where n is 8, 24, 36, 48, etc. These alkali metal-graphites are air- and water-sensitive but are stable as suspensions in tetrahydrofuran, diethyl ether, or pentane for at least 24 h at room temperature. Our work has mainly concerned C_8K , a compound schematically shown below (the dotted spheres in the drawing represent potassium atoms in the interlamellar spaces of a graphite lattice).⁴ The descriptive

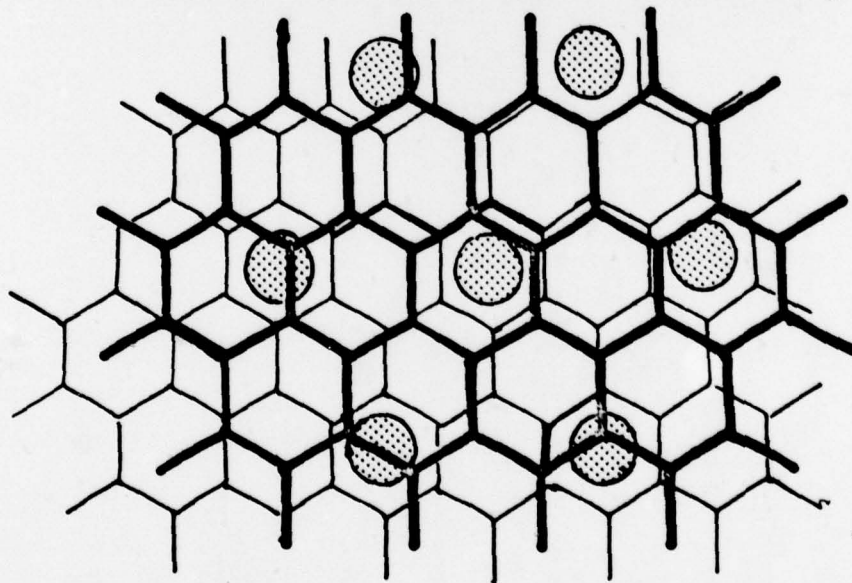
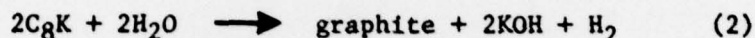
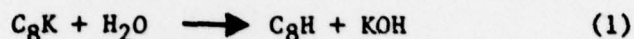


Figure 1. Schematic representation of potassium-graphite (C_8K) showing intercalated potassium.

chemistry of potassium-graphite has been discussed in an earlier article and in essence combines aspects of potassium metal and

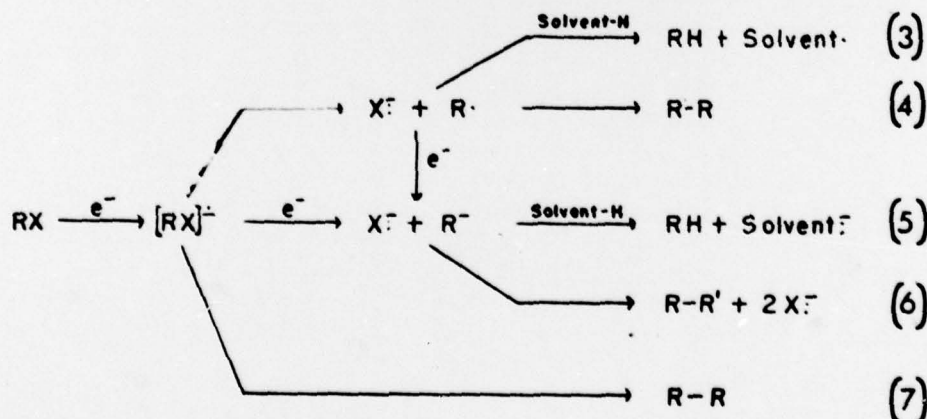
soluble alkali metal aromatic radical anions.⁵ Relevant details of this chemistry are described below.

As we have previously described,⁶ potassium-graphite reacts in THF with weak protic acids like water and alcohols according to equations 1 and 2 with reaction 1 being the predominant reaction.



Although the Lewis acid-base reaction described by equation 1 does predominate with smaller alcohols and water, significantly more reduction (hydrogen evolution, equation 2) is seen with larger alcohols or in reactions run in less polar solvents (diethyl ether or pentane). In most cases, some hydroxide or alkoxide remains in the product graphite as shown by ESCA and can only be removed under rather vigorous conditions by hot aqueous acid or refluxing ethanol. Similar adsorption or intercalation of transition metals has also been noted.⁷⁻⁸ The other alkali metal-graphites, C_8Cs and C_8Rb were briefly studied and showed similar acid-base chemistry.

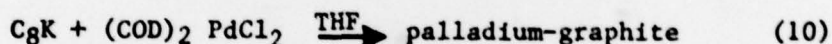
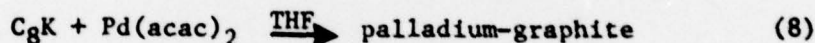
The reducing ability of potassium-graphite noted in equation 2 has been reported previously for both organic and inorganic reactions.⁹⁻¹¹ Our mechanistic studies of C_8K focused on reduction of alkyl halides. The products observed were in general accord with the reactions illustrated in equations 3-7 below. These re-



ductions plausibly occur through radical or radical-like intermediates and evidence for such intermediates was obtained from the experimental observation of 65% cyclization in reduction of 5-hex-enylbromide to methylcyclopentane. This rearrangement is well preceded in other radical reactions and thus constitutes good evidence for radical intermediates.¹² No evidence was obtained for appreciable alkylation of graphite by any alkyl halides, a result which suggested that functionalization of graphite by conventional electrophilic substitution reactions known for soluble

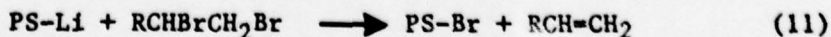
alkali metal aromatic radical anions would not be possible.¹³

Our attention then turned to direct reactions between soluble metal complexes and potassium-graphite. The earlier report of intercalation of cyclopentadienyl complexes of transition metals in graphite led us to initially attempt the reactions between CgK and bis(cyclopentadienyl)titanium dichloride as a route to an active catalyst. However, this reaction failed to yield an active hydrogenation catalyst, apparently because of reduction of titanium(IV) before intercalation could occur.¹⁴ Reactions of potassium graphite with palladium(II) complexes were more successful. Several different palladium(II) complexes were allowed to react with potassium-graphite according to equations 8-10. The products of these reactions were then examined for catalytic activity toward 1-octene



using hydrogen at atmospheric pressure and room temperature. In general, these graphite products were unreactive as hydrogenation catalysts if excess potassium-graphite was used. However, if the reaction mixture (which was a suspension) was quenched with methanolic hydrogen chloride, hydrogenation activity was observed. Typical activity was comparable to 5% palladium on graphite¹⁵ but was somewhat greater than commercially available palladium intercalated in graphite.¹⁶ Our preliminary studies have provided us with no information about the nature of the catalysts we have prepared (i.e. intercalated palladium vs. supported palladium).

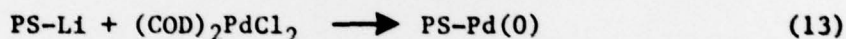
Lithiated polystyrene is a more commonly used polymer for the preparation of immobilized homogeneous catalysts. It is typically prepared by halogen-metal exchange,¹⁷ exchange of soluble lithium reagent with mercurated polystyrene,¹⁸ or by simple deprotonation of polystyrene by TMEDA complexed butyllithium.¹⁹ We have generally found the first of these procedures to be the most convenient. Although this metalated polymer has been widely used as an intermediate in the synthesis of derivatives of polystyrene, satisfactory analytical procedures for analysis of such a reactive polymer are not generally available. During the course of our work we have found that quenches of lithiated polystyrene with a vicinal dibromoalkane can be useful as an analytical procedure. Such a reaction (equation 11) yields one equivalent of alkene for every



PS = polystyrene

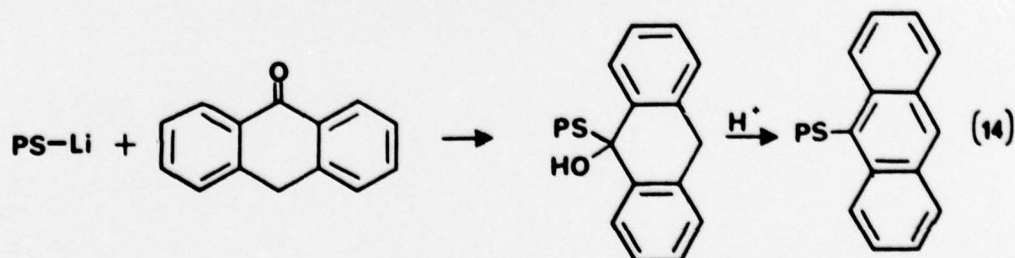
equivalent of active organolithium reagent present and forms the basis of a gas chromatographic analysis of lithiated polymers. This reaction has the further advantage of being able to in principle distinguish between polymeric organolithium and adsorbed organolithium reagents since adsorbed organolithium reagents would be expected to yield a soluble by-product (e.g. butyllithium adsorbed on lithiated polystyrene yields equal amounts of 1-bromobutane and alkene in a reaction like equation 11).

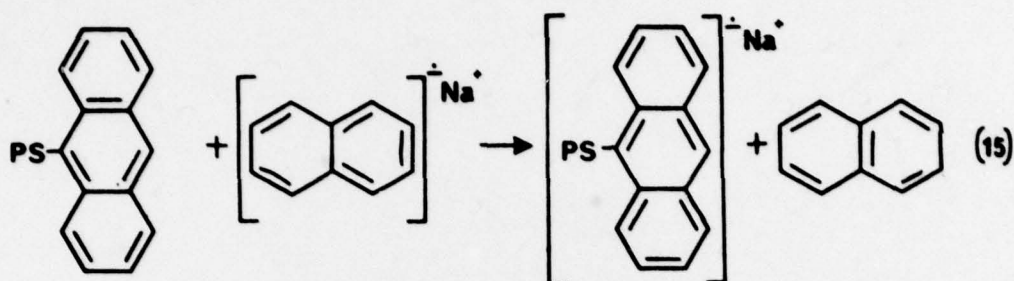
In preliminary experiments, we have found that lithiated polystyrene which our analytical procedures show to be essentially free of *n*-butyllithium can be converted into hydrogenation catalysts using reactions like those of equations 12-13. When phos-



phine complexes of palladium chloride such as bis(tri-*n*-butylphosphine)palladium(II) chloride were allowed to react with excess polystyryl lithium a polystyrene bound palladium(II) species apparently formed. Although this first formed species was not active as a hydrogenation catalyst, appreciable activity was observed if the Pd(II) was first reduced with a hydride reducing agent. Similar catalytic activity was observed for the product of reaction of bis(cyclooctadienyl)palladium(II) chloride and polystyryl lithium. Detailed studies of the catalytic reactions observed for these palladium/polystyrene catalysts are continuing.

Recently we have also been able to prepare a third type of metalated polymer which has some similarity to both an alkali metal-graphite and lithiated polystyrene. Specifically, we have bound a polycyclic aromatic compound to polystyrene using the chemistry described in equation 14 and have then reduced it with a THF solution of sodium naphthalene according to equation 15. Formation of this metalated polystyrene radical anion is indicated by the rapid decolorization of the THF solution of sodium naphthalene and formation of a greenish polymer. Although the resulting polymer bound aromatic radical anion has not yet been fully character-





ized, we have succeeded in using this polymeric organometallic reagent to prepare supported catalysts using reactions directly analogous to equations 12 and 13. We have specifically observed significant hydrogenation activity for such a catalytic species toward 1-octene at room temperature and atmospheric pressure and are now investigating reactions with other substrates.

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